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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

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In a recently published investigation upon the atomic weight of nickel we gave three series of results, depending upon the ratios of silver and of argentic bromide to nickelous bromide.* These led us to the conclusion that the atomic weight in question could not be far from 58.69 if oxygen is 16.000. Since however no single method is ever convincing, and since the results above mentioned did not represent all that might be done even with one method, it was evidently advisable to pursue the matter to a more definite conclusion. Accordingly, we determined to continue the work with a twofold object in view: first, to study further the preparation of pure material, and secondly, to complete the analysis of nickel bromide in such a way as to *determine directly the amount of nickel as well as the amount of bromine in the salt.* No surer test of a quantitative result than such a complete analysis is known. The careful study of all the conditions and results has led us to the conclusion that the preparation of pure nickelous bromide is an unusually difficult problem; but the problem has been so nearly solved that we know exactly the precautions and corrections necessary to make this substance serve as an accurate basis for the determination of the atomic mass of nickel. In the light of this later knowledge we find that the results of the last paper need a slight correction, but it is satisfactory to note that the change amounts to not much over one unit in the second decimal place of the atomic weight.

While carrying out the work, we had continually in mind the various controversies which have arisen over the atomic weights of nickel and

* These Proceedings, XXXIII 97.

cobalt; and feeling that the "Gnomium" question raised by Krüss and Schmidt had never been conclusively laid at rest, we naturally dwelt especially upon it. Unfortunately, one cannot enter into a discussion of this subject without directly antagonizing many views which have been expressed on one side or the other; but of course the following results are recorded solely in the interests of truth, without controversial bias.

The balance and weights used in the work described were the same as those described in the former paper. The weights were re-standardized, with results very similar to those found a year before. All weighings of nickelous bromide were reduced to the vacuum standard by the addition of 0.114 milligrams per gram to the observed weight. The specific gravity of nickel (about 8.7) is so near the specific gravity of brass (8.4) that the correction of the nickel to the vacuum standard is less than one part in a hundred thousand, hence it may be omitted.

Experiments concerning the Purity of the Materials.

The purification of our nickelous material has already been described at length.* Most of the work described below was done with nickel which had been purified by Mond's process and many subsequent operations (Sample III.†), but two analyses were made with a somewhat less pure sample (No. II.†) made from commercial material. Since we had proved that further protracted treatment produced no effect on the combining weight, evidently these specimens were quite pure enough for our purpose.

Krüss and Schmidt used glassware in their preparation work, therefore it seemed worth while to make an exact observation of the well known danger involved in this practice. To this end two very carefully treated specimens of spongy nickel were prepared, one having been made wholly in platinum, and the other wholly in the best Bohemian glass, which had been thoroughly steamed. The former of these preparations, which was supposed to be absolutely pure, left upon sublimation as bromide in a stream of bromine vapor only a very minute siliceous residue. The specimen of nickel which had been prepared in glass vessels was totally different in appearance from the one prepared in platinum; instead of being metallic and coherent, it was black and powdery. Upon the conversion of about ten grams of this dark powder into nickelous bromide, a beautifully iridescent voluminous residue, weighing about five milligrams and consisting mainly of silica, was left in the boat. Evi-

* These Proceedings, XXXIII 102.

† Ibid., 105.

dently this silica had prevented the cohering or "sintering" of the metal during its original reduction from the oxide, and hence caused the pulverized state of the impure metal, — a fact which is interesting as showing the great change in properties produced by a small amount of impurities.

These two experiments emphasize the well known facts that glass is wholly unsuitable for accurate work, and that material prepared even in platinum is extremely difficult to render wholly free from silica, unless it is vaporized.* While however our purest *nickel* sometimes contained traces of silica, the *bromide* prepared from it by sublimation was undoubtedly as free as possible from this impurity. Further light upon this question will be given in a following paper upon cobalt.

Although a possible contamination with silica was thus little to be feared, some other constituents of glass or porcelain were much more dangerous. All the material actually used in our analyses had been prepared wholly in platinum vessels at every stage excepting at the very end, when it had been sublimed in a porcelain tube. Obviously this tube might be attacked by the hot mixture of hydrobromic acid, bromine, and nickelous bromide vapor; but since nothing beside sodic bromide would probably sublime with the nickelous salt, and the "equivalent" of sodic bromide is almost equal to that of nickelous bromide, the slight impurity could produce no important effect upon our last year's work. This was realized at the time; and the discovery of the presence or absence of this error was one of the prearranged objects of the present paper. Since the work recorded below was completed, Professor Winkler, by a kind personal letter as well as by a recent article, wisely called attention to this flaw; and it will be seen that his objection had been both substantiated and answered before he wrote about it.

The easiest method of detecting sodic bromide in nickelous bromide is obviously to reduce the latter and then to extract the former with water from the spongy metal. Moist hydrogen easily divorces the halogen from its none too stable metallic union at a temperature of not much over 300°, at which temperature sodic bromide is essentially non-volatile. In this way repeated experiments showed that all our nickelous bromide had contained on the average not far from one tenth of one per cent of sodic bromide. The particulars concerning the determination of this serious impurity naturally form an essential point in the method of analysis of the nickel salt, hence they will be found later under that head.

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* Compare Stas's "Untersuchungen" (Aronstein), pp. 269 and 279.

The presence of an unreduced bromide was first detected by Mr. Baxter in the course of his work on cobaltous bromide, and some interesting details involved in its discovery will be recorded in the paper upon that subject. The amount present varied with the temperature used in the sublimation, but was otherwise surprisingly constant. The concurrent sublimation of the two salts is undoubtedly similar to the distillation of organic substances with steam, sodic bromide possessing a small constant vapor-tension at the constant temperature of about 900° used in the sublimations.

After the completion of a series of reductions of nickelous bromide containing this impurity of sodic bromide, a final attempt was made to obtain the salt of nickel in a state of absolute purity. We expected that platinum would be attacked by the mixture of bromine vapor, hydrobromic acid, and nickelous bromide, which exists in the red-hot tube during the sublimation of the salt, but platinum is the last resort in cases of this kind. In order to sacrifice as little of the precious metal as possible in our desperate experiment a large porcelain tube was lined with platinum foil,* and inside of this was placed a platinum boat containing the metal to be converted into bromide. In each of two separate specimens of nickelous bromide made in this apparatus merely a trace of sodium was found, but unfortunately enough platinum was present to render the results valueless. They are not included in the tables below. Only a small strip of the foil was injured, the very hot parts and the cool parts being alike untouched. After these experiments we abandoned the attempt to prepare absolutely pure nickelous bromide, and returned to the use of the porcelain tube for the sublimations; for sodium is an impurity much more easily weighed than platinum, under the circumstances. The only method of obviating the difficulty would have been to use a tube of nickel for the sublimation; but the obtaining and moulding of a large amount of the metal in a perfectly pure state promised to be so troublesome that we have not yet attempted this improvement.

The arrangement for supplying and purifying the large volumes of hydrogen needed in this research was gradually evolved from the simple form used in the first experiments to an elaborate piece of apparatus which will be described in detail in the paper upon cobalt.

The preparation of bromine and of the other materials has been de-

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* This idea was suggested by Professor H. B. Hill. Compare also Penfield, Zeitschr. Anorg. Chem., VII. 22.

scribed in sufficient detail in other papers,* so that no further words need be wasted upon these points. It is almost unnecessary to state that in these simple operations no loophole was left open through which an error might creep in to destroy the value of the more difficult undertaking before us. We are indebted to the Cyrus M. Warren Fund for Chemical Research in Harvard University for some of our more expensive pieces of apparatus.

The Method of Analysis.

At first many attempts were made to determine nickel by electrolysis, with the hope that nickelous bromide might be analyzed in this simple and direct fashion. In order to test the method, weighed amounts of the purest spongy metal were dissolved and reprecipitated electrolytically. The spongy metal had been prepared by boiling the purest platinum-made ammonio-nitrate with much water, igniting and reducing the precipitate with pure ammonia, and heating the metal in a vacuum. The weight of nickel deposited by electrolysis always exceeded that of the pure nickel taken, hence the electrolytic method was abandoned as unsuitable for work of the highest accuracy. The excess of weight, which was noticeable even when the film was heated to 120° before weighing, and often exceeded two tenths of one per cent when it was dried at 50° after the method of Winkler,† was traced to inclusion of mother liquor between the film and the dish, and to the probable presence of occluded hydrogen in the nickel.‡ Since the deposit was beautifully metallic and coherent in appearance, one might well have expected a better result. It is possible that these observations may help to explain Winkler's high values for the atomic weight of nickel and cobalt, since he used the electrolytic method. On the other hand, the *spongy* metal which had been used in our experiments was probably purer than that prepared in any other way, for solid impurities had been rigorously excluded, and the traces of gas present had been pumped out.

These preliminary experiments showed that the best method of determining the amount of nickel in the bromide would be to reduce it in a stream of hydrogen, provided that the reduction could be accomplished without the loss of any of the bromide by volatilization. Following in the footsteps of Mr. Baxter's work with cobalt, it was found that moist

* These Proceedings, XXXIII. 106 *et seq.*

† Zeitschr. Anorg. Chem., IV., 22.

‡ Raoult, Compt. Rend., LXIX. 826; Böttger, Dingler's Polytech. Journ., CCI. 80 (1871).

hydrogen answered the purpose; for the temperature at which the reduction takes place is so low that no trace of nickel was found outside of the boat which originally contained the bromide, if a rapid current of the gas was maintained. It is obvious that according to the law of mass-action, the presence of a large proportion of hydrobromic acid resulting from the reduction would tend to prevent the desired reaction, and hence to facilitate the undesired sublimation; therefore a large excess of hydrogen must be present. Of course the hard glass tube used for this process was always afterwards treated internally with nitric acid, and the liquid was examined with minute care for traces of nickel.

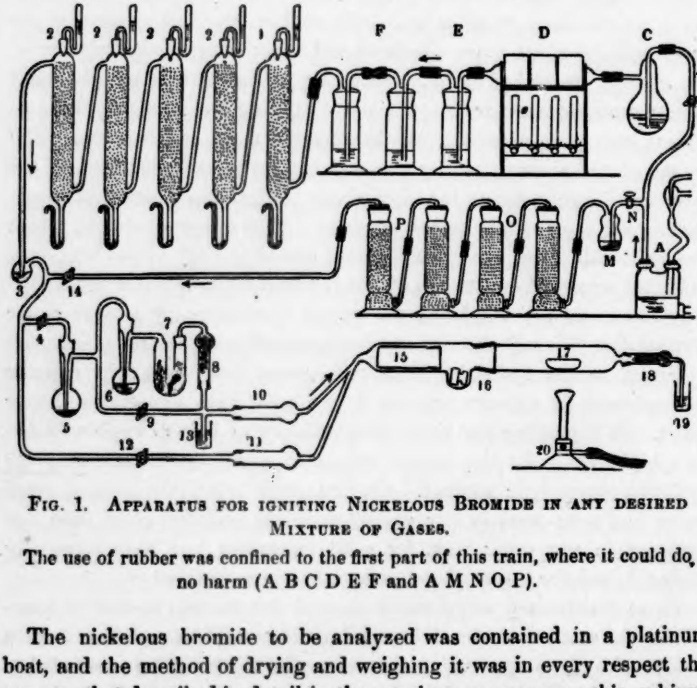

Fig. 1. Apparatus for igniting Nickelous Bromide in any desired Mixture of Gases.

The use of rubber was confined to the first part of this train, where it could do no harm (A B C D E F and A M N O P).

The nickelous bromide to be analyzed was contained in a platinum boat, and the method of drying and weighing it was in every respect the same as that described in detail in the previous paper upon this subject. After having been weighed, the boat was carefully placed in a hard glass tube, in which the bromide was cautiously reduced to the metal. When the reduction was completed and the apparatus had just cooled, the boat and its contents were returned to their weighing bottle, where they were enclosed in an atmosphere of dry air. The weight of the residue was

found after half an hour, and then at the end of many hours. Since the boat was cool before having been introduced into the bottle, two successive weighings thus made never differed from one another by amounts beyond the limit of error of weighing. Spongy nickel evidently does not oxidize in dry air.

It is obviously a matter of great importance to discover whether or not the material prepared in this way contains weighable amounts of occluded hydrogen. According to the experiments of Neumann and Streintz* who worked with reduced metals, two cubic centimeters of the gas were occluded by each gram of spongy nickel. This amount would alter the observed atomic weight by only about the fortieth of one per cent; but since we are aiming at even greater accuracy, the matter should evidently be probed to the bottom.

In the first place, carefully weighed nickel remaining from one of the analyses recorded below was ignited in a Sprengel vacuum at perhaps 550°. For fear of losing some sodic bromide a higher temperature could not be employed. No appreciable loss of weight occurred and no gas was evolved during this process, which was repeated with several specimens; hence there seemed to be good reason to believe that no hydrogen was occluded by the metal in our experiments. In order to prove the matter, one and a half grams of spongy nickel reduced from the bromide and allowed to cool in hydrogen was oxidized by heating in a current of dry air, which was subsequently passed over red hot cupric oxide, and through a carefully weighed tube containing phosphoric oxide. Since the absorption tube did not gain in weight, no water could have been formed during the combustion, and hence no hydrogen could have been occluded.

Treated in exactly the same way, four grams of nickel prepared by the reduction of the *oxide* yielded about three milligrams of water, or about half the amount found by Neumann and Streintz. This agreement is sufficient to show that these investigators were not mistaken in their conclusions, and that the permeability of nickel is enormously modified by minor circumstances.

Is the presence of the sodic bromide, otherwise so objectionable, the agency which prevents the occlusion in our case, or does the volatility of nickelous bromide allow its metal to be deposited in a form more coherent than that remaining from the oxide? The attempt to answer these

* Monatshefte für Chemie, XII. 640 (1891). Berichte der d. ch. Gesell., XXV., 1872.

questions experimentally would be far from uninteresting, but it is sufficient for the present purpose to prove in the manner described above that nickel treated as we have treated it in the following determinations does not occlude an important amount of hydrogen, and does not oxidize in dry air. Confirmatory evidence will be found in the paper upon cobalt which follows.

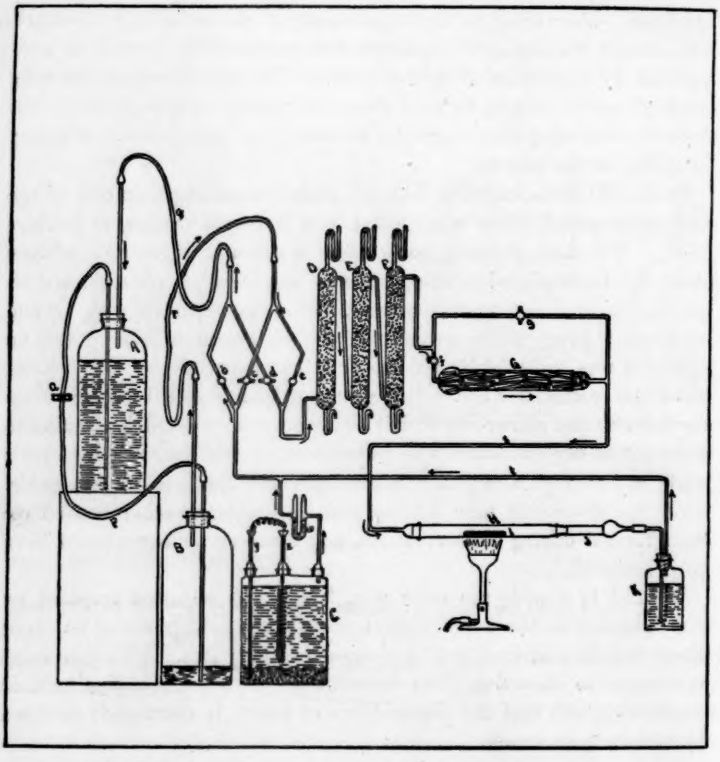

FIG. 2. APPARATUS FOR REDUCING THE BROMIDE.

Before it was possible to use the data thus obtained for the calculation of the desired atomic mass, the weight of sodic bromide existing as impurity within the spongy metal must obviously be found. Accordingly the residue was digested with successive portions of pure water in a platinum dish, and the bromine in the filtrates was precipitated and weighed as

argentic bromide. Since the spongy metal (after slow solution in very dilute nitric acid in a platinum dish) was found to contain no bromine, it is safe to infer that all the soluble impurity had been leached out by the water. This process was repeated with every analysis, the result being always the same. From the weight of argentic bromide thus obtained, the weight of the impurity of sodic bromide was alculated, and when this quantity was subtracted from both the original weight of the nickelous bromide and the weight of the spongy metal, data suitable for the calculation of the atomic mass were obtained.

In order to show that this method of correcting the results is really exact, it is necessary to prove, first, that no impurity other than a bromide remains behind in the nickel, and secondly, that no impurity beside sodic bromide is dissolved by the water. The first point has been already partially considered; we have shown that silica at least was absent.* Since silica was the only non-volatile and insoluble acid likely to have been present, and all the bromine had been dissolved out by water, the only probable impurities were other metals capable of being reduced from their bromides by hydrogen. But these, even if they had been present in unsuspected and undiscoverable traces, could have exercised no appreciable effect upon the atomic weight unless their equivalents were widely different from that of nickel. Hence this possibility of error need cause no anxiety. Finally, it has been already stated that no weighable amount of hydrogen was ever found in the metal, hence we are justified in the assumption that the washed out spongy nickel is a safe material upon which to base the calculation of the atomic mass in question.

The question as to the purity of the sodic bromide in the wash-waters was a matter less easily settled. Careful qualitative and quantitative analysis of the liquid were alone capable of deciding the point, and with only infinitesimal amounts of material such elaborate examination was difficult. To make a very long story short, nothing was found in any of the wash-waters beside sodium, bromine, nickel, and in some of the earlier analyses traces of sulphuric acid. This last impurity may have crept in from the air during the evaporation of the aqueous solutions, or possibly from the towers used for drying the nitrogen and air. In the later analyses sulphuric acid was not used in these towers, and was proved to be absent from the nickelous bromide. As its amount was in any ease very small, we felt justified in neglecting it as one neglects an infinitesimal of the second order in the course of mathematical reasoning.

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* See p. 328.

On the other hand, the amounts of nickel in the wash-waters were distinctly weighable, and not to be overlooked. That it was nickel, and not a new metal, there could be no room for doubt; for it gave a black sulphide and a green sulphate, the characteristic pink coloration with potassic thiocarbonate, as well as a beautiful rose-colored flame test, which we have found to be characteristic of nickelous halides. Since the nickel salts are much more easily reduced than those of cobalt (see the next paper), it is harder to obtain a satisfactory flame test in the former case than in the latter. Only when both salts and gas are *dry*, and the vaporization proceeds in the inner flame, are the best results to be obtained. We have found no reference to this flame reaction of nickel halides in chemical literature,* and one cannot but believe it to have been unknown to Krüss and to Winkler at the time of one of their disputes.†

The question now arises, Whence came this nickel? Was it occluded as nickelous bromide in the interior of crystals of sodic bromide, and thus protected from reduction, or was it dissolved as hydroxide from the spongy metal? The large quantity of nickel present seemed to overthrow the former alternative, but the possibility of the latter is emphatically denied by Winkler,‡ and rejected after some hesitation by Krüss.§ Since the equivalent of nickelous bromide is very near that of sodic bromide (109.3 : 103), and the impurity was calculated from the amount of bromine present, the point has no important bearing on the immediate problem; but nevertheless it is always interesting to settle a mooted question of this sort.

Winkler's experiments were made with coherent nickel coated on the inside of a platinum dish, while Krüss's experiments were made with spongy metal in porcelain vessels. The former found no trace of any substance in the water in which his nickel had been digested, while the latter found a large residue (most of which must have come from the porcelain), and hastily ascribed this residue to the presence of an unknown element. It

* Vogel, Spectral Anal. irdischer Stoffe, pp. 246, 262.

† Krüss and Schmidt, Zeitschr. Anorg. Chem., II. 249; Winkler, Ibid., IV. 17. Krüss observed the appearance of a pale rose-colored flame during the ignition of his nickel in a Rose crucible in hydrogen, accompanied with a loss of weight. If the hydrogen was *dry*, and especially if, as is often the case, it contained traces of hydrochloric acid, minute traces of nickelous chloride might have been sublimed and have caused this phenomenon, which Krüss ascribed to "gnomium" and Winkler ascribed to potassium. This question is worthy of further attention.

‡ Winkler, Zeitschr. Anorg. Chem., IV. 12.

§ Krüss, Zeitschr. Anorg. Chem., II. 238.

is not at all impossible that, in spite of the well known permanence of the smooth bright surface of a nickel-plated object, the spongy metal reduced by hydrogen might be easily oxidized and dissolved.* The difference in this respect between polished iron and the same metal reduced by hydrogen is well known. Hence Winkler's experiments prove nothing with regard to the behavior of finely divided nickel. The position of nickel on the positive side of hydrogen in the electro-chemical series leads one to expect that it must behave as zinc and iron do, although to a less degree.†

In order to decide the matter so far as the present work is concerned, we sought to determine experimentally, first, if the purest water is capable of acting on the purest nickel, and secondly, if the hydroxide thus formed is slightly soluble in water. To settle the first point, some very pure reduced nickel was thoroughly washed with water, and then digested at 20° for some time with repeated portions of water just purified. In every case nickel could be found in the filtrate, both by means of potassic thiocarbonate and by evaporation to dryness. Many repetitions of the experiment with new samples of metal brought always the same result. It is quite possible that galvanic action hastened this oxidation, for of course the nickel was contained in a platinum dish. Since Winkler's dish was evenly coated, the water probably did not touch the platinum in his case, and hence this possible cause of acceleration was absent; but the difference between the smooth surface and the finely divided surface alone is amply sufficient to explain the difference in the speed of the reaction.

It will be remembered that Krüss, in one of his experiments, digested a mass of nickel for a year on the steam bath with water, and obtained a white residue which was the chief basis of his alleged discovery. Our work shows that this residue must have contained not only dissolved porcelain, but also enough nickel to yield the black sulphide, the pale green color, and the electrolyzed metal which led Krüss so far astray.

* It is a peculiar household fact that cold water faucets plated with nickel are usually less brilliant than their hot water comrades; this difference may well be ascribed to the slow action of condensed water, even upon polished nickel. The greater tendency to rust shown by cobalt may well be due to the fact that in its case the hydroxide is converted into a higher state of oxidation immediately upon being dissolved, thus giving opportunity for the solution and hence for the formation of more hydroxide. In the case of nickel the thin permanent film of $Ni(OH)_2$ probably protects the metal, although its solubility may be no less than that of $Co(OH)_2$.

† See a paper entitled "Autoxydation," by R. Ihle, Zeitschr. phys. Chem., XXII. 114.

It is clear that, since no acid was present in the water, *the nickel must have been dissolved in the form of hydroxide.* In none of our experiments with the purest metal did the solution give an alkaline reaction with phenol phthaleïn, hence hydroxyl ions must be absent, and the hydroxide must be dissolved in a colloidal form. The alkaline reaction sometimes observed by Krüss and Winkler must have been due to impurities, as Winkler pertinently suggests. Traces of alkali would surely be found in nickel oxide precipitated in glass vessels, even when mercuric oxide was used as the precipitant.

Nickelous hydroxide, precipitated by alkali and thoroughly washed, possesses at least as great solubility as the hydroxide which is formed by the slow oxidation of nickel. Upon suitable electrolysis, fifteen cubic centimeters of such a *cold* solution yielded 0.00062 gram of nickel, while another similar portion yielded 0.00057 gram, or about 0.04 gram per litre. Since the solubility is a colloidal one, its limit is indeterminate; hence no elaborate attempt was made to discover its exact amount. It is well known that the presence of other salts in the solution diminish this kind of solubility, but the small amount of sodic bromide present in this case was insufficient to produce any considerable effect. Undoubtedly the fact that the solubility is colloidal and uncertain is responsible for the conflicting statements of the various authorities and handbooks.*

This solubility of nickelous hydrate is the circumstance which obliged us to determine the residue of sodic bromide through argentic bromide, instead of simply by evaporating the wash-waters poured off from the nickel and weighing the residue. This necessity is made clear by the following table.

No. of Anal.	Weight of Nickel.	Weight of Residue extracted by Water and dried at 105°.	Weight of AgBr.	Weight of NaBr calculated from AgBr.	Weight unaccounted for.
	grams.	grams.	grams.	grams.	grams.
6	0.805	0.00330	0.00410	0.00225	0.00105
7	1.488	0.00895	0.01398	0.00767	0.00128
8	0.607	0.00400	0.00568	0.00311	0.00089

In order to prove that this large percentage of unexplained residue

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* Finkener (Handbuch der Anal. Chem. von Rose, 6te Auflage von Finkener, II. 136); Busse (Zeitschr. Anal. Chem., XVII. 60); Fresenius (Quant. Anal., 1877–1887, II. 393, 823); Roscoe and Schorlemmer (A Treatise on Chemistry, Vol. II. Part II. p. 149); Winkler (*loc. cit.*); Krüss (*loc. cit.*); etc. Temperature is a circumstance which produces great effect on this kind of solubility, heat being apt to coagulate the dissolved material.

consisted chiefly of nickelous hydrate, two more determinations were made with new material. Since enough data for the atomic weight had been obtained, and time pressed, the bromide of nickel was not weighed in the first place. In these analyses the *nickel* dissolved as hydroxide was also weighed.

Weight of Residue obtained, dried at 105°.	Argentic Bromide found.	Nickel deposited electrolytically.	Sodic Bromide calculated.	Nickelous Hydroxide calculated.	Total calculated Weight of Residue.	Weight unaccounted for.
grams.	grams.	grams.	grams.	grams.	grams.	grams.
0.00925	0.01405	0.00092	0.00770	0.00146	0.00916	0.00009
0.00480	0.00630	0.00084	0.00345	0.00133	0.00478	0.00002

Besides this quantitative proof that the residue consisted of nothing but sodic bromide and nickelous hydrate, many qualitative analyses had shown the absence of lime, alumina, silica, and even potash, from the solution poured off from the reduced nickel. Traces of sulphuric acid were found, as has been said, only in the first specimens.

In the light of all these results, no doubt seemed to remain as to the proper mode of correcting the direct gravimetric results of the reduction. Obviously the weight of the sodic bromide must be subtracted from the weights of both the nickelous bromide and the metal formed from it by the action of the hydrogen; for the salt existed in each. On the other hand, the nickelous hydroxide was simply to be neglected; for this substance was formed after the last weighing had been finished. The temperature used for the reduction was so low that no sodic bromide was vaporized; at least none could be found in the cooler parts of the reduction tube.

Analyses 5 and 6 were made with nickelous bromide of the grade of purity represented by the numeral II. in the former paper, while all the others were made with that labelled III., which had been made through the carbonic oxide process. The headings of the various columns will show with sufficient clearness the meanings of the figures given below.

In this series of results, the lowest is 58.696, while the highest is 58.719, a variation ± 0.012 from the mean. Adding all the determinations together, 24.31725 grams of nickelous bromide yielded 6.52286 grams of pure washed nickel and 0.02778 gram of sodic bromide, calculated from 0.0507 gram of argentic bromide. These two weights, taken in connection with the amount of bromine found a year ago, furnish a

THE ATOMIC WEIGHT OF NICKEL.

FOURTH SERIES. — O = 16. — RATIO = $NiBr_2$: Ni.

No. of Anal.	Sample.	Weight of Nickel Bromide in Vacuum.	Weight of Nickel in Vacuum.	Weight of Sodium Bromide to subtract.*	Weight of Nickel Bromide corrected.	Weight of Nickel corrected.	Atomic Weight of Nickel.
		grams.	grams.	grams.	grams.	grams.	
1	III.	2.83610	0.76366	0.00285	2.83325	0.76081	58.705
2	III.	3.21908	0.86641	0.00283	3.21625	0.86358	58.696
3	III.	2.31578	0.62431	0.00337	2.31241	0.62094	58.703
4	III.	2.88330	0.77707	0.00377	2.87953	0.77330	58.710
5	II.	2.29843	0.61872	0.00193	2.29650	0.61679	58.719
6	II.	2.99118	0.80497	0.00225	2.98893	0.80272	58.714
7	III.	5.52058	1.48823	0.00767	5.51291	1.48056	58.716
8	III*a*.	2.25280	0.60726	0.00311	2.24969	0.60415	58.710
						Average	58.709

complete analysis of the best nickelous bromide which we were able to prepare. It must be remembered that 15.51556 grams of the halide contained, according to two different methods, 11.34985 and 11.34979 grams of bromine.

COMPLETE ANALYSIS OF NICKELOUS BROMIDE.

			Per cent.
Nickel		=	26.824
Total Bromine = 73.151% =	Bromine combined with Nickel	=	73.062
Total Impurity = 0.114% =	Bromine actually found in impurity	=	0.089
	Sodium	=	0.025
	Total	=	100.000†

* The weights of argentic bromide from which the sodic bromide was calculated were respectively 0.00520, 0.00516, 0.00615, 0.00687, and 0.00352 grams in analyses 1, 2, 3, 4, and 5. For analyses 6, 7, and 8, the figures are given on p. 338.

† As has been detailed, some of the earlier preparations contained traces of sulphuric acid in addition. Since this is not taken into account in the average, the sum given is slightly too small, and is perhaps deceptive in its accurate showing. The flaw was eliminated as soon as it was discovered, therefore we had no means

It has been already pointed out that this impurity of $\frac{1}{40}$ per cent of sodium would make no difference in last year's results if the "equivalent" of sodium equalled that of nickel. Since, however, it is somewhat less, slightly too much argentic bromide was obtained last year, and the atomic weight of nickel appeared lower than it really is. Assuming the amount of impurity to have been the same in last year's preparation as in this, 0.015 should be added to the atomic weight, in order to correct this error. The results of the four series, which represent the sum and substance of the present research, are then as follows. Ratios (*e*) and (*f*) were obtained by cross-reckoning from the earlier ratios. The reason for thus restating the results is because this restatement uses the weight of the nickelous bromide only as a constant, and not as a basis of calculation.

			Atomic Weight of Nickel if O = 16.000.
(*a*)	Preliminary: 2 AgBr	: $NiBr_2$	[58.695]
(*b*)	2 AgBr	: $NiBr_2$	58.703
(*c*)	2 Ag	: $NiBr_2$	58.704
(*d*)	($NiBr_2$ — Ni)	: Ni	58.709
[(*e*)]	2 AgBr	: Ni	58.706
[(*f*)]	2 Ag	: Ni	58.707
			59.706

If any assurance is needed that this average indicates very nearly the true atomic weight of nickel, the assurance may be found in the review of older work which follows. This review has been postponed until the close of the paper, in order that the methods might be judged in the light of our own experience with the subject.

A Brief Criticism of Earlier Work.

The atomic weights of nickel and cobalt have each been the subject of a score of different researches since the problem was first attacked by Rothoff in 1818. These investigations have not only led to exceedingly discordant results, but have also given rise to several interesting and important controversies. As a chronological list is given in our former papers,* there is no need of repeating it here. For the purpose of

of finding the exact amount of the sulphuric acid, but in any case it was so small as to produce only a negligible effect on the result. From some experiments of Mr. Baxter's it is safe to assume that this error could not have exceeded 0.005 per cent in the worst cases, and in the average it must be still much less.

* These Proceedings, XXXIII. 97, 115.

criticism one should rather classify the investigations according to the methods used in them.

The most direct method of determining the atomic weight of nickel is obviously the reduction of nickelous oxide, for in this way the ratio between nickel and oxygen, the usually accepted standard of atomic weights, is settled at once. Russell, Zimmermann, Mond Langer and Quincke, Schützenberger, and Krüss and Schmidt * used this method with varying degrees of success. Of these five investigations the third was hastily undertaken only to show that nickel which has been vaporized as nickelcarbonyl is essentially similar to the ordinary material; the fourth included only two determinations made with oxide undoubtedly containing traces of sulphate, and the last was hopelessly faulty for reasons already discussed. Hence as exact criteria we may reject these three at once, and turn back to the much more carefully executed work of Russell and Zimmermann.

Russell showed that when the higher oxides of nickel and cobalt are ignited in an inert atmosphere, oxygen is driven off and the monoxide remains. His materials were contained in a Rose crucible of platinum; and after igniting the oxides in a stream of carbon dioxide, he reduced them in a stream of hydrogen. His nickelous oxide was very carefully freed from all extraneous matter except the insidious impurities derived from his glass vessels, against which no precautions were taken. A careful study of his work shows that this is the most serious cause of error likely to affect his final result, but that it was probably in part counteracted by the presence of occluded gases in the oxide; hence we have good reason to believe that this result is probably somewhat, but not much, too high.

Zimmermann followed essentially the same method as Russell. From ten exceedingly concordant analyses he deduced the value 58.694† for nickel, a value slightly lower than Russell's 58.743. His work also was carried out with great care, and the effort was made to avoid the occlusion of alkaline impurities by precipitating the final hydroxide of nickel

		Result.
* 1863	Russell, Jour. Chem. Soc., [2], I. 51,	Ni = 58.743
1886	Zimmermann, Annalen (Liebig's), CCXXXII. 324,	Ni = 58.694
1890	Mond, etc. Jour. Chem. Soc., LVII. 753,	Ni = 58.580
1892	Schützenberger, Compt. Rend., CXIV. 1149,	Ni = 58.515
1892	Krüss and Schmidt, Zeitschr. Anorg. Chem., II. 235,	Ni = 57.5 to 64. (!)

† Krüss and Alibegoff, who published Zimmermann's result, after his death, unwisely omitted to apply the correction to the vacuum standard. This omission has been supplied above.

with pure oxide of mercury, thus doing away with the use of an alkaline precipitant. This improvement also lessened the danger of Russell's other chief error, and at the same time introduced yet another with an opposite tendency, the inclusion of mercury; hence it is not surprising that his result should be somewhat the lower of the two. An unprejudiced critic cannot but consider Zimmermann's work as the best among the older researches, and it is pleasant to call attention to the fact that Zimmermann's result differs by only the fiftieth of one per cent from ours. The reason why this method gives a result more satisfactory in the case of nickel than in that of cobalt is probably because cobaltous oxide is so much more readily raised to the higher stage of oxidation. Both Russell's and Zimmermann's work may have been slightly vitiated by the presence of occluded hydrogen in their nickel; but it is impossible now to appraise the error involved, because the phenomenon is so irregular.

It is convenient to class together five more investigations which appeared between 1857 and 1871.* In the light of present knowledge concerning the possibilities of accurate quantitative work these contributions may be dismissed with few words. Marignac showed that Schneider's oxalate contained occluded impurities, and Schneider showed that Marignac's chloride could hardly have been both anhydrous and free from oxide. Our own experience entirely confirms both of these criticisms. Dumas's lack of ability to determine chlorine with accuracy throws out his analyses of the chloride at once, even if one is credulous enough to believe that the choride itself was pure. Sommaruga precipitated sulphuric acid from nickelous potassic sulphate as baric sulphate, a method now ostracised except for crude work. Lee's work was wonderfully accurate, considering the small quantities of materials which he used, but these quantities were so microscopic, and his compounds were so complex, that one could not have been expected to improve much upon his error of one per cent without a radical reformation of method.

Within this same period appeared another paper by Russell, elaborated as carefully as his previous one, but depending upon a less satisfactory process. The hydrogen evolved by the action of nickel upon hydrochloric acid was measured. Many uncertainties combine to make this

* (1857)	Schneider, Pogg. Annal., CI. 387, CVII. 616,	58.07
(1858)	Marignac, Arch. Sci. Nat., (nouv. sér.), I. 375,	58.90
(1860)	Dumas, Annalen (Liebig's), CXIII. 25,	59.02
(1866)	Sommaruga, Sitzber. Wien. Acad., LIV. [2], 50,	58.03
(1871)	Lee, Am J. Sci., [3], II. 44,	58.01

method of little value, so that the result (58.77 ?) does not carry with it much weight.

Three chemists in three different decades, Marignac, Baubigny, and Schützenberger,* have attempted to solve the question by the quantitative ignition of nickelous sulphate. The three investigations agreed fairly well upon an average result, 58.71,† Baubigny's being by far the most satisfactory. This method is one involving two errors which nearly counterbalance each other: — the sulphate has a tendency to retain water, while the oxide almost invariably retains sulphuric acid. For this reason, the method gives results which approximate closely to the truth.‡ Here again we have a support for the conclusion that the value in question cannot be far from 58.7.

All the published work upon the subject has now been referred to except some early work of Rothoff, Erdmann and Marchand, and Deville § (which deserves no more than a passing mention), and the more recent researches of Winkler. Krüss's misguided work has been sufficiently dissected by Winkler's able but unsparing criticism ‖ and in the experimental part of this paper. The only points not covered by Winkler, — the rose-colored flame test and the solubility of nickelous hydrate, are explained in the foregoing pages.

The work of Winkler is surprising in its variety and in the ingenuity of his methods, but unfortunately it is equally surprising in the wide range of one per cent between his several results. His earliest work,** depending upon the reduction of sodic aurochloride by nickel, giving the extremely high value 59.45, is obviously at fault. Winkler himself ignores it in his discussion,†† so that further criticism of it may well be omitted.

Winkler's two later investigations, carried out only a few years ago, gave results much lower and more satisfactory. In his first revision he weighed nickel, converted it into chloride, and determined the chlorine

			Greatest Difference from Mean.
* (1858)	Marignac, Arch. Sci. Nat., (nouv. sér.), I. 374,	Ni = 58.70	± 0.15
(1883)	Baubigny, Compt. Rend., XCVII. 951,	Ni = 58.73	± 0.002
(1892)	Schützenberger, Compt. Rend., CXIV. 1149,	Ni = 58.65	± 0.075

† Clarke, Recalculation, top of page 302.

‡ See "A Table of Atomic Weights," These Proceedings, XXXIII. 297, 298.

§ See Clarke, Recalculation, p. 291.

‖ Zeitschr. Anorg. Chem., IV. 10.

** 1867. Zeitschr. Anal. Chem., VI. 18. Ni = 59.45 (Clarke).

†† Zeitschr. Anorg. Chem., IV. 10, VIII. 1.

both gravimetrically and volumetrically.* He wisely regulated his operations in such a way as to avoid the use of alkalis; but in his ardor to escape this danger he encountered others as serious. It is highly unlikely that the electrolytic nickel, dried at only 50° while adhering to the dish, could have been free from impurities, as we have already shown in the experimental part of our paper. Indeed, he confessed in a later paper † that the electrolysis of cobalt at any rate is very far from being as accurate a process as it is sometimes supposed to be. The report of the acid reaction of the chlorides of these metals would have had more significance if the indicator had been named, for the salts destroy the magenta of phenol phthalein only because they remove the hydroxyl ions from the solution. Both chlorides are perfectly neutral to methyl orange. A loss of chlorine during the drying of either chloride would of course raise the observed atomic weight; and while in the case of nickel the loss was so small as not to have produced a visible cloudiness, no proof is offered that no loss took place. In the case of the cobalt "eine gewisse, aber so schwache Trübung, dass sie, wie man zu sagen pflegt, nicht 'blank' erschien" involved a loss of as much as one per cent of material, and it is well possible that a smaller but still important amount of basic salt may have escaped notice in the case of the nickel. Our own experience with the halides of both metals convinces us that it is quite impossible to obtain them pure and dry by evaporating to dryness in moist air. Turning now to the determination of the chlorine in the salts, we find other grave flaws. No account was taken of the solubility of argentic chloride in the gravimetric work, and several milligrams must have been washed away by the hot dilute nitric acid used as a washing fluid. One is surprised, too, to find that the antiquated process of burning the filter was adopted, instead of Gooch's admirable substitute. In the volumetric work again the solubility of argentic chloride was overlooked, although it produces a most injurious effect on the method of Volhard.‡ It is indeed surprising to see so eminent a chemist using volumetric methods at all in this way, for every one knows the difficulty of obtaining results of a very high grade of accuracy by their aid. In this laboratory the burette is only called into use when at least ninety-nine per cent of the material has been weighed out, and then only a few cubic centimeters of a very dilute solution are added to

* Zeitschr. Anorg. Chem., IV. 10, 1893.

† Zeitschr. Anorg. Chem., VIII. 4.

‡ These Proceedings, XXVI. 34, and XXIX. 67.

complete the quota. This is quite a different story. It is evident that nearly all the errors mentioned tend to make Winkler's result too high.

Some singular oversights appear also in the calculation of the results. For example, in one place Winkler compares 0.1662 gram of nickel with 0.6079206 gram of silver. The small amount of nickel was deposited in a large platinum dish, and its weight could certainly not have been determined more accurately than within 0.1 milligram, hence at least three decimal places of the recorded weight of silver were superfluous, even if the volumetric solution could have been prepared with an error of only one part in six millions. It is perhaps well to mention also that his final results, varying in the case of cobalt from 59.5996 to 59.7480 (if $O = 15.96$) are given as far as four decimal places.

While a review of this work is necessary in order to explain why the results should be too high, perhaps one should not be severe in one's criticism of it, for Professor Winkler himself rejects it, as well as some later work on cobalt,* in his most recent contribution upon the subject.† In this new paper he pins his faith to another series of determinations made in 1894, with a very ingenious method adopted after sundry fruitless attempts in other directions. It behooves us then to consider this later work with great care.‡

Evidently many of the errors which render the older investigation untrustworthy were eliminated from that of the subsequent year. The nickel was separated from the platinum dish and afterwards ignited in an atmosphere of hydrogen, and the solubility of argentic chloride does not enter into the question. On the other hand, the unfortunate use of volumetric operations and the misuse of figures remained, while to these were added other dangers not present in the older work. The ingenious procedure was as follows: pure nickel was acted upon by pure iodine, and the excess of iodine was determined by sodic thiosulphate. Many text-books upon volumetric analysis name the process of iodometry as one of the most accurate of titrimetric methods simply because the end point is an extremely sharp one. In reality, the lack of permanence of the necessary solutions render it distinctly unsuitable for very accurate work even under the best conditions. When the iodine must

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* Zeitschr. Anorg. Chem., IV. 462.

† Zeitschr. Anorg. Chem., XVII. 236.

‡ 1894 (1895), Winkler, Zeitschr. Anorg. Chem., VIII. 1, 291; $Ni = 58.85$. It must be borne in mind in referring to Winkler's papers that he uses the old standard $O = 15.96$. His values have all been translated into the more convenient notation ($O = 16.000$) in this paper.

remain in solution for twenty-four hours after weighing and before titration, and when this circumstance is complicated by the presence of a metal capable of acting to a slight extent even upon pure water in the presence of air, one can hardly contend that the conditions are the best. The chance of side reactions seems to be too great to admit of infallibility in the results. One is surprised, indeed, that Winkler's results approach as near to those of Zimmermann as they do, and this close approach is evidence of great accuracy of manipulation on Winkler's part. In short, viewed from the standpoint of ordinary analytical experience, Winkler's last work is admirable, while from the standpoint of atomic weight research it is inadmissible. In justice to Professor Winkler it is only fair to add that he realizes this fact himself.* One need not dwell upon possible inaccuracies, however; for Winkler himself has furnished us with data for computing the error of his method. In a short paper he uses the same method for determining the atomic weight of iron, and finds for this quantity the value 56.174, if O = 16.000.† Now according to the fairly consistent work of Berzelius, Erdmann and Marchand, Svanberg and Norlin, and Maumené, the atomic weight of iron cannot be far from 56.02; and there is no contradictory evidence of serious value.‡ Winkler's method then gave him a result 0.275 per cent § too high in the case of iron, and it is fair to conclude that the error could not have been far different in the case of nickel. Making the corresponding subtraction, Winkler's corrected result approaches astoundingly near to those obtained by Zimmermann and by us.‖

Winkler's corrected value	58.69
Zimmermann's value	58.694
Richards and Cushman's value	58.706
Average	58.70

Owing to a slight uncertainty in the atomic weight of iron, as well as to the possibility that iron may behave somewhat differently from nickel

* Zeitschr. Anorg. Chem., XVII. 239.

† Zeitschr. Anorg. Chem., VIII. 291.

‡ Clarke's recalculation, p. 289. The atomic weight of iron is now being further studied in this Laboratory.

§ It is possible that a small part of this error is due to the omission of the reduction to the vacuum standard, which would affect the final value by about 0.01 per cent. This correction may have been applied, but there is no evidence of such application.

‖ Mr. Baxter first called our attention to this remarkable unanimity.

in iodine solutions, this comparison is less significant than it seems to be; but certainly it does not militate *against* our value for the atomic weight of nickel. It is of interest to note that Clarke's mathematical method of selecting from among the older values led to the number 58.687.

Professor Winkler's sixth and last paper upon this subject appeared only last summer, after the work described in this paper had been completed.* In it he kindly points out several possible flaws and omissions in our earlier paper. This criticism will be discussed at length in the next paper on cobalt.

CAMBRIDGE, MASS., October 22, 1898.

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* Zeitschr. Anorg. Chem., XVII. 236.